STRUCTURE AND PROPERTIES OF BASE EXCHANGE MATERIALS

BY
BERNARD FRED DUDENBOSTEL, JR.
B.S., University of Illinois, 1938

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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STRUCTURE AND PROPERTIES OF BASE EXCHANGE MATERIALS

THEORETICAL

A. Distribution-Equilibrium in Ion Exchange.

An ion exchanger is a solid substance which reversibly interchanges the ions present on the solid with other ions present in a liquid phase. Several equations have been proposed[1] to represent this process of ion exchange. Some of these are empirical, but most are merely variations of the simple law of mass action. However, none take into account the ion activities of either the ions in solution or the ions adsorbed on the solid exchanger; or the necessary modification of the simple mass law for univalent ions when divalent ions are present.

Since most known data seem to fit the simple mass action equation as well as any, it may be assumed that a modification of this equation to include ion activities and the effects of the presence of divalent ions might more nearly express the phenomenon of ion exchange. Thus, letting

MR = exchanger saturated with M^+ cations,

$M'R$ = exchanger saturated with M'^{++} cations,

δ = ion activities,

K = equilibrium constant, and

m = molalities of solutions;

$2\,MR + M'^{++} = M'R_2 + 2\,M^+$, represents the true mass law expression for ion exchange, which may be written:

$$\left(\frac{m_{M'^{++}} \cdot \delta_{M'^{++}}}{m^2_{M^+} \cdot \delta^2_{M^+}}\right)_{\text{solid}} = K \cdot \left(\frac{m_{M'^{++}} \cdot \delta_{M'^{++}}}{m^2_{M^+} \cdot \delta^2_{M^+}}\right)_{\text{solution}}$$

Ion activities in solution are well known, but no values are known for ion activites of ions on solids. Hence, unit activites were used for the latter.

B. Hydration and Ion Exchange.

A corollary of the modern theory of valence was proposed by Latimer and Rodebush[2] which proposed the hydrogen bond as an explanation of the valence in certain compounds. This suggestion offers a plausible explanation of the way in which many substances combine with water since they have oxygen or nitrogen atoms with free electron pairs which could share one of the hydrogen atoms of water. Previous work[3] has shown that infrared spectroscopic studies show two bands which can be assigned definite frequencies. Thus, the 2.75 mu band is the unbonded or free --OH and the 2.92 mu band is the bonded --OH (hydrogen bond). X-ray investigations[4, 5, 6] have indicated two types of water combination in montmorillonite, one of which was supposed to result in the formation of --OH groups. Present data agree with X-ray investigations and identify the second water linkage as occurring through the hydrogen bond.

The variation in the amount of water taken up by the various montmorillonites may be related to an actual difference in water required by the various cations for isomorphous replacement as occurs in the zeolites.

C. Electrodialytic Regeneration of Ion Exchangers.

The removal of electrolyte from a colloid in dialysis is accelerated by the application of an electric current; this is electrodialysis. Varying with the charge of the membrane, a current of water moves from one electrode to the other, most generally from the anode to the cathode, and this carries the products of the electrolysis into the intermediate cell.

Using this process, it is possible to produce a hydrogen saturated material in the intermediate cell. This may be expressed by:

$$NaR + H_2O \overset{e}{=} HR + Na^+ + OH^-$$

where NaR = solid exchanger saturated with sodium ions.
HR = solid exchanger saturated with hydrogen ions,
e = process of electrodialysis.

Results and Discussion

A. Distribution-Equilibrium in Ion Exchange.

Saturation capacities were determined on each of three synthetic aluminosilicate exchangers for 0.005, 0.025, 0.05, 0.25, and 0.50 molal solutions of $CaCl_2$, $BaCl_2$, and $MgCl_2$ by complete exhaustion in a column.

The equilibrium constants were determined by shaking known amounts of each exchanger with each of the above solutions in sealed tubes at a constant temperature of 25.0 ± 0.1C. until equilibrium was reached. The amount of exchange at equilibrium was determined by analysis of the solution at equilibrium.

Using the above values as determined, known ion activites for ions in solution, and unit activites for ions on the solid in the above equation; the equilibrium constants were calculated.

Up to ionic strengths of about 0.025, the reaction seemed to fit the above expression quite well, as is shown below:

	Calcium Chloride					*Barium Chloride*					*Magnesium Chloride*				
Ionic Strengths	*.007*	*.014*	*.025*	*.05*	*.10*	*.007*	*.014*	*.025*	*.05*	*.10*	*.007*	*.014*	*.025*	*.05*	*.10*
						Equilibrium Constants									
Doucil	7.7	4.3	1.6	.33	.17	68.	72.	239.	6.4	2.9	18.6	16.5	6.5	1.3	.35
Fed. Min.	8.8	3.2	1.2	.43	.17	108.	125.	255.	4.9	5.6	26.2	21.1	8.2	1.4	.56
Crystallite	6.4	6.1	6.6	.35	.22	114.	100.	292.	6.4	5.5	14.8	11.2	1.1	0.9	.40

Above 0.025, a sharp break is noted, indicating that the assumed ionic activity coefficients of unity for ions on the solid exchanger are incorrect at high concentrations. However, the concept of activity fails in practicability in this region.

B. Hydration and Ion Exchange.[7]

The infrared absorption studies were made with a spectroscope built in this laboratory in 1936.[8]

From these studies we can place the montmorillonites saturated with the various cations (Ca^{++}, Mg^{++}, Li^{+}, K^{+},

Ba^{++}, H^+, Na^+, and NH_4^+) into four classes with respect to water uptake. The first class, one of extreme absorption, consists of the Ca^{++} and Mg^{++} montmorillonites. The second, of appreciable absorption, consists of the Li^+, K^+, and Ba^{++} montmorillonites; and the third class, H^+ and Na^+ montmorillonites, was one of slight absorption. The fourth, consisting of NH_4^+ montmorillonite, showed almost no change on attempted hydration.

The NH_4^+ montmorillonite showed a doublet at 3.13 and 3.27 mu characteristic of the NH_4^+ halides, which have a doublet at 3.20 and 3.30 mu.

Similar studies of clays of low base exchange capacity indicate that less bonded (2.92 mu) and unbonded (2.75 mu) --OH is present than in the case of the higher base exchange montmorillonites.

The assignment of the 2.75 mu band to the unbonded --OH frequency is corroborated experimentally. Clays allowing replacement of structural --OH by phosphate show about 25 per cent less absorption at 2.75 mu than do unphosphated clays.

X-ray data show that the artificial gel zeolites are definitely amorphous while glauconite is crystalline in structure. X-ray data also show that the increased base exchange capacity of greensand after heat treatment may be due to the formation of new particles.

C. Electrodialytic Regeneration of Ion Exchangers.

A Mattson electrodialysis cell[9] was used to form hydrogen exchangers. A graphite anode and copper cathode were used, employing 110 D. C. at an amperage of 0.15 and a temperature of less than 50°C. Exhaustion capacities of the exchangers were determined in columns by the standard procedure.[10]

Folin's Permutit formed no hydrogen exchanger; heating destroyed its capacity. Federal Mineral (a synthetic aluminosilicate), a raw greensand, and a carbonaceous exchanger (Nalcite A) were successfully regenerated by this method and run through two cycles of exhaustion and regeneration.

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VITA

Bernard Dudenbostel was born in St. Louis, Missouri, on April 12, 1917. He attended grammar school in Christopher, Illinois. From 1931-1934 he attended the Christopher Community High School. He attended Southern Illinois State Normal University at Carbondale from 1934-1936; then transferred to the University of Illinois where he received the degree of Bachelor of Science in 1938. He then entered the Graduate School of the University of Illinois where he studied physical and inorganic chemistry and physics. He held an assistantship in chemistry made possible by the Illinois State Water Survey from July, 1938, to October, 1940, and from July, 1941, to February, 1942. From October, 1940, to July, 1941, he held a National Defense Research Council fellowship. He is a member of Pi Kappa Phi, Sigma Xi, Chemeka, and Phi Lambda Upsilon. A thesis (B. S.) was written in 1938 on the subject "New Reactions in Water Treatment." He has one paper which has been published, "Spectroscopic Studies of Base Exchange Materials," J. Am. Chem. Soc., *63*, 2554 (1941), in collaboration with A. M. Buswell. Also a 53 page report was presented to the National Defense Council which is not available for publication.